Sediment Physical and Chemical Characterization

by Jennifer Nelson-Lee

Introduction

Chemical and physical characterization of the subsurface is essential for establishing the spatial distribution and concentrations of the contaminants present and to more fully demonstrate effects of and mechanisms involved in the remediation process at the Gasoline Spill (GS) area both prior to and following Dynamic Underground Stripping (DUS) activities. In order to facilitate effective characterization, a sampling and analysis plan must be assembled to ensure representative field samples in the treatment area. The sampling and analysis plan also needs to provide data for mass balance estimates of in situ soil contaminant concentrations. Continuous well logging during drilling activities helped in providing a better understanding of the lithology at the study site.

Procedures

Field Procedures

Drilling and Completion Methods

A total of 37 boreholes were used in the characterization effort for the Dynamic Underground Stripping project. Both hollow stem auger and mud rotary drilling methods were employed during the characterization phase. Some boreholes were completed as piezometer (B or P) and monitoring boreholes (TEP, HW, TOM), while others were completed as injection wells (IW) and extraction wells (EW). Each borehole took approximately one week to completely drill and sample. Table 1 contains a summary of borehole descriptions and sampling data. The type and location of the boreholes in the gasoline spill (GS) area appear in Figure 1.

Sampling Procedure

During all characterization efforts, sampling plans included lithology descriptions on continuous core during drilling, retrieval of core samples with depth for determination of contaminant concentrations, and selected retrieval of core samples for various physical and biological measurements. A detailed sampling plan utilized during the characterization phase post-DUS activities appears in Appendix C.

Sampling Team

A number of people participated with the sampling effort so that there would be overlap during the long hours of drilling, and to facilitate the smooth running of the laboratories in which these people were also working. Also included in the team were personnel representing the EPA who participated in the sampling of two of the six post DUS characterization boreholes. The actual members of the sampling team are recorded in Appendix C of this report.

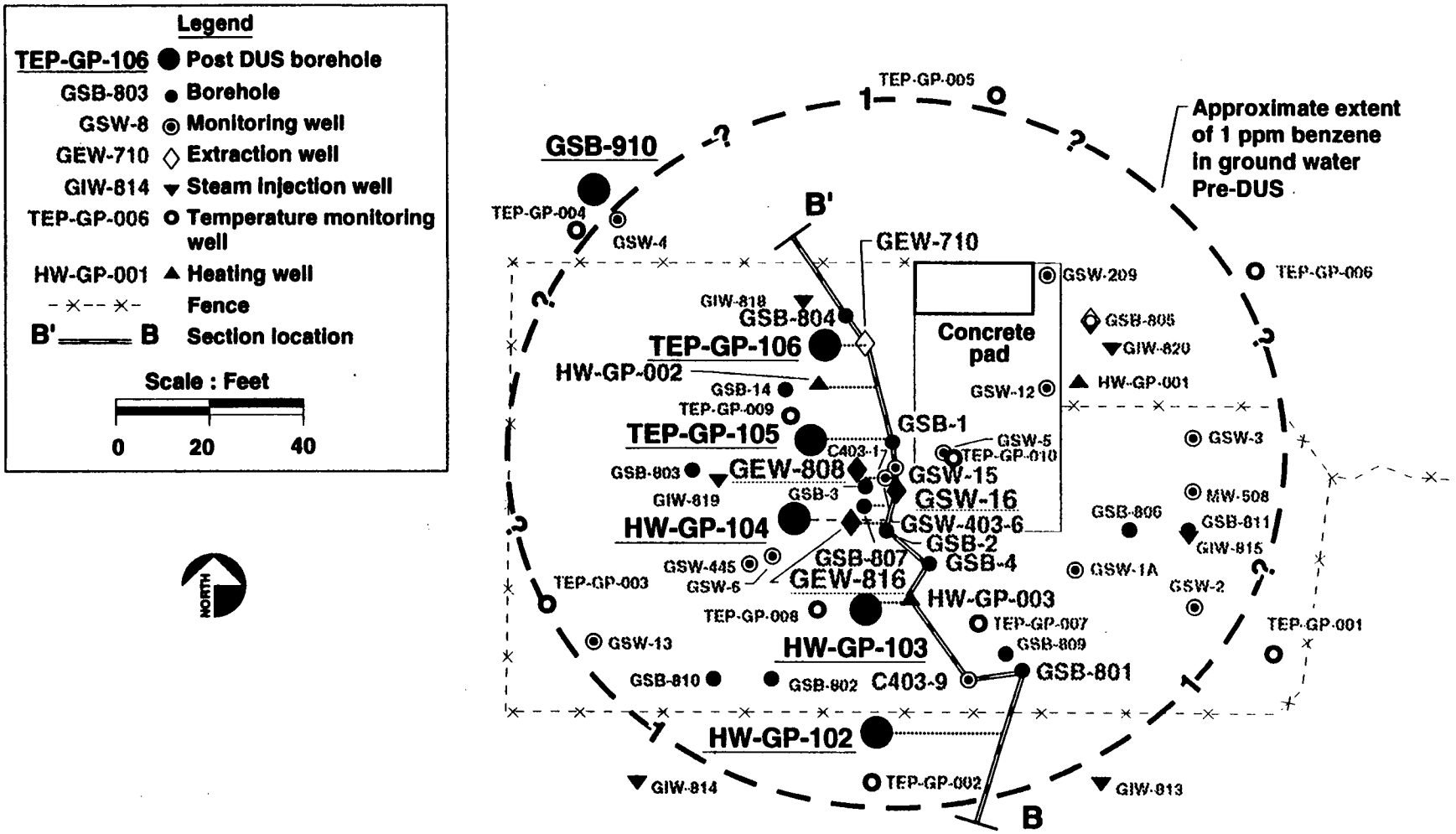

Figure 1. Location of boreholes at the Gasoline Spill Site.

Table 1. Description of boreholes drilled at Gasoline Spill Site Study Area

Well Number	Date borehole started	Borehole depths (ft)	Date well completed	Casing depths (ft)	Drilling geologist	Drilling Method	Annulus (in)	Water table depth (ft)	Cored interval (ft)	Sampled interval (ft)	Total # soil samples collected	Type of analyses	Sampled zone	Sampling method	Sample size (in)	
SVB-GP-008A	10/23/90	90.0	11/2/90	90.00	JCM	Hollow stem auger (HSA)	12.00	N/A	0 - 90	27 - 89	239	Chemistry Bacteriology Physical *Kd Extra	90u 14u 24u 73u 38u	Lateral and vertical brass liner inserts	2.5 x 3.0 1.5 x 3.0	Samp latera cores
SVB-GP-013	2/25/91	90.0	3/11/91	90.00	JCM	HSA	12.00	N/A	0 - 90	N/A	211	Chemistry Bacteriology Physical *Kd Extra	105u 21u 26u 39u 20u	Lateral and vertical brass liner inserts	2.5 x 3.0 1.5 x 3.0	GE lo Hollo core v
SVB-GP-014	3/13/91	90.0	3/27/91	90.00	JCM	HSA	10.00	N/A	0-90	N/A	244	Chemistry Bacteriology Physical *Kd Extra	120u 40u 18u 54u 12u			Hollo GE lo Incre side v
GSB-710	5/14/91	150.0	**5/17/91	Not cased	SCN	HSA	9.00	100.5	1-140	4-138	193	Chemistry Bacteriology Physical *Kd Extra	21u 15s 35u 17s 45u 23s 9u 2s 14u 5s	Lateral brass liner inserts		Later Field
GSB-711	5/20/91	150.0	**5/24/91	Not cased	SCN/JCM	HSA	9.00	103.00	1-150	2-124	85	Chemistry Bacteriology Physical *Kd Extra	38u 10s 17u 4s 0u 4s 0 9u 4s	Lateral brass liner inserts		Hollo Boreh Field
GSB-801	12/17/91	143.9	12/23/91	127.50	SCN	HSA	8.00	117.50	0-130	1-144	215	Chemistry Bacteriology Physical *Kd Extra	38u 15s 44u 18s 51u 19s 16u 6s 0	Lateral brass liners		Hollo Boreh logbo
GSB-802	12/11/91	148.0	12/20/91	128.00	SN/JM	HSA	8.00	103.30	0-148	2-148	263	Chemistry Bacteriology Physical *Kd Extra	44u 31s 34u 41s 50u 38s 14u 11s 0	Lateral brass liners		Hollo drilli
GSB-803	4/24/92	150.0	4/27/92		SCN	HSA	8.00	105.10	1-150	2-145	46	Chemistry Bacteriology Physical *Kd Extra	4u 13s 0 0 0 8u 21s	Lateral brass liners		Field

Table 1. (Continued.)

Well Number	Date borehole started	Borehole depths (ft)	Date well completed	Casing depths (ft)	Drilling geologist	Drilling Method	Annulus (in)	Water table depth (ft)	Cored interval (ft)	Sampled interval (ft)	Total # soil samples collected	Type of analyses	Sampled zone	Sampling method	Sample size (in)	Comments
GSB-804	2/6/92	145.5	2/12/92	140.00	SCN/JCM	HSA	8.00	119.70	0-146	2-145	219	Chemistry Bacteriology Physical *Kd Extra	56u 12s 0 97u 8s 22u 3s 18u 3s	Lateral and vertical brass liners		Field logbook GH-053
GSB-805	2/27/92	150.0	3/2/92	143.50	JCM	HSA	8.00	101.70	0-150	0-150	184	Chemistry Bacteriology Physical *Kd Extra	37u 18s 0 59u 25s 16u 7s 15u 7s	Laterally and vertically punched holes	2.5 x 3.0	Field logbook GH-110
GSB-806	2/21/92	140.0	2/25/92		JCM	HSA	8.00	120.20	0-140	0-140	138	Chemistry Bacteriology Physical *Kd Extra	36u 5s 0 58u 7s 15u 3s 13u 1s	Lateral and vertical brass liner inserts	2.5 x 3.0	Field logbook GH-097
GSB-807	3/4/92	150.5	3/9/92	150.00	JCM	HSA	8.00	120.50	0-151	5-149	273	Chemistry Bacteriology Physical *Kd Extra	50u 17s 64u 16s 65u 21s 18u 5s 12u 5s	Lateral and vertical brass liner inserts	2.5 x 3.0	Field logbook GH-130
GSB-808	2/13/92	150.0	2/20/92		JCM	HSA	8.00	121.00	0-150	4-148	224	Chemistry Bacteriology Physical *Kd Extra	50u 8s 50u 4s 62u 10s 19u 3s 15u 3s	Lateral and vertical brass liner inserts	2.5 x 3.0	Field logbook GH-075
GSB-809	1/27/92	141.0	1/30/92	140.00	JCM	HSA	8.00	115.50	0-141.5	N/A	N/A	Chemistry Bacteriology Physical *Kd Extra	0 0 0 0 0	N/A	N/A	No soil samples taken. Field logbook GH-036
GSB-810	2/3/92	151.5	2/5/92		JCM	HSA	8.00	110.30	0-150	N/A	N/A	Chemistry Bacteriology Physical *Kd Extra	0 0 0 0 0	N/A	N/A	No soil samples taken. Field logbook GN-067
GSB-811	3/10/92	140.1	3/16/92	140.00	JCM	HSA	8.00	119.50	0-140	11-140	92	Chemistry Bacteriology Physical *Kd Extra	28u 4s 0 27u 14s 6u 3s 16u 4s	Lateral and vertical brass liners	2.5 x 3.0	Field logbook GI-018
TEP-GP-001	1/13/92	165.0	1/21/92	160.50	SCN	HSA	11.50	105.50	0-165	4-165	231	Chemistry Bacteriology Physical *Kd Extra	39u 22s 52u 24s 45u 27s 14u 8s 0	Lateral and vertical brass liners	2.5 x 3.0	Field logbook GH-005

Table 1. (Continued.)

Well Number	Date borehole started	Borehole depths (ft)	Date well completed	Casing depths (ft)	Drilling geologist	Drilling Method	Annulus (in)	Water table depth (ft)	Cored interval (ft)	Sampled interval (ft)	Total # soil samples collected	Type of analyses	Sampled zone	Sampling method	Sample size (in)	Comments
TEP-GP-003	1/22/92	161.1	1/28/92	161.10	SCN/JM	HSA	11.50	105.00	0-161	5-159	176	Chemistry Bacteriology Physical *Kd Extra	32u 31s 0 43u 27s 13u 11s 11u 8s	Lateral and vertical brass liners	2.5 x 3.0	Field logbook GH-013
TEP-GP-004	1/30/92	161.0	2/5/92	106 &134	SN	HSA	11.50	104.40	0-161	4-160	242	Chemistry Bacteriology Physical *Kd Extra	39u 22s 42u 24s 50u 25s 13u 8s 13u 6s	Lateral and vertical brass liners	2.5 x 3.0	Field logbook GH-033
TEP-GP-005	2/6/92	161.0	2/18/92	161.00	CJ/SN	HSA	11.50	108.00	0-161	4-160	154	Chemistry Bacteriology Physical *Kd Extra	35u 14s 0 51u 19s 11u 6s 10u 8s	Lateral and vertical brass liners	2.5 x 3.0	Field logbook GH-54, Drill Rig Malfunction see GH-63
TEP-GP-006	2/19/92	161.0	2/26/92	161.60	SCN	HSA	11.50	112.90	0-161	3-161	211	Chemistry Bacteriology Physical *Kd Extra	34u 18s 46u 22s 45u 17s 12u 6s 6u 5s	Lateral and vertical brass liners	2.5 x 3.0	Field logbook GH-88
TEP-GP-007	3/6/92	161.0	3/13/92	161.00	SCN	HSA	11.00	109.00	0-161	13-157	71	Chemistry Bacteriology Physical *Kd Extra	14u 1s 13u 1s 31u 0s 6u 0s 4u 1s	Lateral and vertical brass liners	2.5 x 3.0	Field logbook GH-001
TEP-GP-008	2/28/92	161.0	3/4/92	161.00	SCN	HSA	11.50	105.20	0-161	13-153	211	Chemistry Bacteriology Physical *Kd Extra	38u 16s 46u 13s 56u 15s 12u 4s 7u 4s	Lateral and vertical brass liners	2.5 x 3.0	Field logbook GH-117
TEP-GP-009	4/29/92	161.8	5/4/92	161.00	SCN	HSA	11.75	102.10	1-162	6-160	48	Chemistry Bacteriology Physical *Kd Extra	4u 9s 2u 10s 0 0 8u 15s	Lateral and vertical brass liners	2.5 x 3.0	Field logbook GI-062
TEP-GP-010	3/17/92	161.0	3/24/92	160.70	SCN	HSA	11.00	109.60	0-161	22-161	239	Chemistry Bacteriology Physical *Kd Extra	44u 32s 30u 20s 51u 25s 13u 7s 11u 6s	Lateral and vertical brass liners	2.5 x 3.0	Field logbook GI-022
TEP-GP-011-01	3/26/92	73.0	**3/27/92	not cased	SCN	HSA	11.75	N/A	0-73	20-67	27	Chemistry Bacteriology Physical *Kd Extra	7u 0 12u 4u 4u	Lateral and vertical brass liners		Drilling problems/abandoned. Field logbook SD

Table 1. (Continued.)

Well Number	Date borehole started	Borehole depths (ft)	Date well completed	Casing depths (ft)	Drilling geologist	Drilling Method	Annulus (in)	Water table depth (ft)	Cored interval (ft)	Sampled interval (ft)	Total # soil samples collected	Type of analyses	Sampled zone	Sampling method	Sample size (in)	
TEP-GP-011-02	3/30/92	57.0	3/30/92		SCN	HSA	11.75	N/A	0-57	N/A	0	Chemistry Bacteriology Physical *Kd Extra	0 0 0 0 0	N/A		Drilling p Field logb
TEP-GP-011-03	3/31/92	161.0	4/7/92		SCN	HSA	11.75	104.50	0-162	90-159	74	Chemistry Bacteriology Physical *Kd Extra	7u 12s 10u 26s 0 2u 8s 2u 7s	Lateral and vertical brass liners		Instrumer measuren Field logb
HW-GP-001	4/14/92	120.0	4/22/92	113.0 &77.0	SCN	HSA	11.75	115.00	0-123	83-119	10	Chemistry Bacteriology Physical *Kd Extra	6u 4s 0 0 0 0	Lateral and vertical brass liners		Upper we Lower we Field logb
HW-GP-002	5/7/92	120.0	5/13/92	78 &117	SCN	HSA	14.00	103.80	0-120	4-119	124	Chemistry Bacteriology Physical *Kd Extra	21u 4s 42u 8s 0 0 41u 8s	Lateral and vertical brass liners		Upper we Lower we Field logb GL-084
HW-GP-003	5/14/92	119.0	5/20/92	119 & 76.5	SCN	HSA	11.75	103.00	1-119	5-100	100	Chemistry Bacteriology Physical *Kd Extra	22u 4s 36u 4s 0 0 30u 4s	Lateral and vertical brass liners		Upper we Lower we Field logb
HW-GP-102	8/4/93	140.0	8/13/93	137.00	SCN/TMH	HSA	8.00	104.40	0-140	41-135	90	Chemistry Bacteriology Physical *Kd Extra	30u 17s 15u 5s 4u 1s 7u 2s 7u 1s	Vertical brass liners	2.5 x 3.0 2.5 x 6.0	Field logb
HW-GP-103	8/16/93	138.0	8/23/93	136.50	TMH	HSA	see (Q)	111.00	1-138	43-129	76	Chemistry Bacteriology Physical *Kd Extra	23u 10s 15u 4s 3u 2s 7u 2s 6u 4s	Vertical brass liners	2.5 x 3.0	Annulus:8 10" OD (2 Annulus (
HW-GP-104	8/24/93	138.0	9/2/93	137.50	TMH	HSA	see (Q)	105.00	0-138	40-132	69	Chemistry Bacteriology Physical *Kd Extra	16u 10s 15u 4s 5u 1s 5u 4s 7u 2s	Vertical brass liners	2.5 x 3.0 2.5 x 6.0	Annulus:p 15"(0-20)}, Field logb
TEP-GP-105	9/21/93	140.0	9/28/93	137.50	TMH	HSA	6.00	113.00	0-166	42-135	98	Chemistry Bacteriology Physical *Kd Extra	43u 9s 0 9u 4s 9u 4s 16u 4s	Vertical brass liners	2.5 x 3.0 2.5 x 6.0	Field logb

Table 1. (Continued.)

Well Number	Date borehole started	Borehole depths (ft)	Date well completed	Casing depths (ft)	Drilling geologist	Drilling Method	Annulus (in)	Water table depth (ft)	Cored interval (ft)	Sampled interval (ft)	Total # soil samples collected	Type of analyses	Sampled zone	Sampling method	Sample size (in)	Comments
TEP-GP-106	9/14/93	137.5	9/21/93	135.50	TMH	HSA	10.50	60 - 61.5	0-166	41-135	81	Chemistry Bacteriology Physical *Kd Extra	12u 13s 14u 5s 7u 5s 6u 5s 9u 5s	Vertical brass liners	2.5 x 3.0 2.5 x 6.0 Loose in carton	Field logbook GN-077
GSB-910	9/3/93	140.0	9/13/93	not cased	TMH	HSA	11.00	68.7-68.8	0-140	40-131	80	Chemistry Bacteriology Physical *Kd Extra	18u 16s 13u 4s 4u 3s 6u 5s 8u 3s	Vertical brass liners	2.5 x 3.0 2.5 x 6.0	Fossil from borehole at 164' Field logbook GN-067

Note:

* samples were also used for physical analyses

** borehole was not as a well

Safety Issues

All personnel involved in the drilling and sampling activities were required to have their SARA/OSHA 40-hour training and the SARA/OSHA 8-hour refresher course where necessary. Sampling team members also had to be respirator fitted, and wear appropriate safety shoes, glasses, hardhats, Tyvek suits (when necessary), and heat insulated gloves while sampling. Team members also needed to be current in the following training courses: HS-4050 and EP-0006 as per OSP 406.2. Additional safety training was provided by Bob Bainer and/or Jerry Duarte on pertinent safety measures and the use of the OVA/OVM at the drilling site.

Sample Collection

Continuous coring and lithological logging were a part of the process used in the characterization boreholes where both the hollow stem auger and mud rotary drilling methods were utilized. However, wherever possible, samples for physical, chemical, and biological analyses were taken using an 18-inch long, 2.5 inch diamter split spoon sampler lined with 6 steam-cleaned brass sleeves. Samples were collected at regular intervals according to the predetermined sampling plan (Appendix C). Typically, samples were collected at 10 foot intervals from the surface through 70 feet. Sampling of the 6 post DUS characterization boreholes started at 40 feet and continued through 70 feet. (The preliminary sampling and analysis results showed little if any BTEX above 40 feet.) From 75 feet to 135 feet, sampling was performed every 5 feet. In some cases, additional biology, chemistry, and "Extra" samples were also taken from continuous core by driving the brass liners into the side of the core using a special teflon adapter and hammer. Additional details of type and frequency of samples appear in Appendix C.

Continuous monitoring was performed using an Organic Vapor Analyzer/ Organic Vapor Meter (OVA/OVM) with a Photoionization Detector (PID) as sediment core was extracted. Organic vapor emission measurements were made by placing a small portion of the sample in a sealed plastic bag with the OVM intake to obtain an indication of where contamination might be present. A field sample log book was used for recording the sample size, type, location and storage, temperature readings, OVA/OVM readings, document control number, and the name of the laboratory performing the analysis. OVA/OVM readings appear with depth in Appendix D. Correlations with laboratory Gas Chromatography (GC) measurements were made by using specially prepared standards that were analyzed by both methods.

Temperature measurements were taken from both split spoon and continuous sediment cores by the insertion of a 0°C-150°C-stainless steel thermometer for field use. The thermometer was driven about 1.5 in. into one end of the 2.5-in.-diameter split spoon sample towards the center and a reading taken after the temperature stabilized (approximately 1 minute later). The temperature of the continuous core was read after inserting the thermometer into the side of the core towards the center. A reading was taken after the temperature appeared to be constant. Figures 2a and 2b illustrate the orientation of the thermometer inserted into the split spoon and the continuous cores respectively. Temperature readings were taken before and after every split spoon sample. Additional readings were taken whenever they were deemed necessary by the head sampler; i.e. from split spoon samples where there was sloughing of the borehole wall, and hence were not good for analytical use. Thus temperatures were taken from sediment cores that

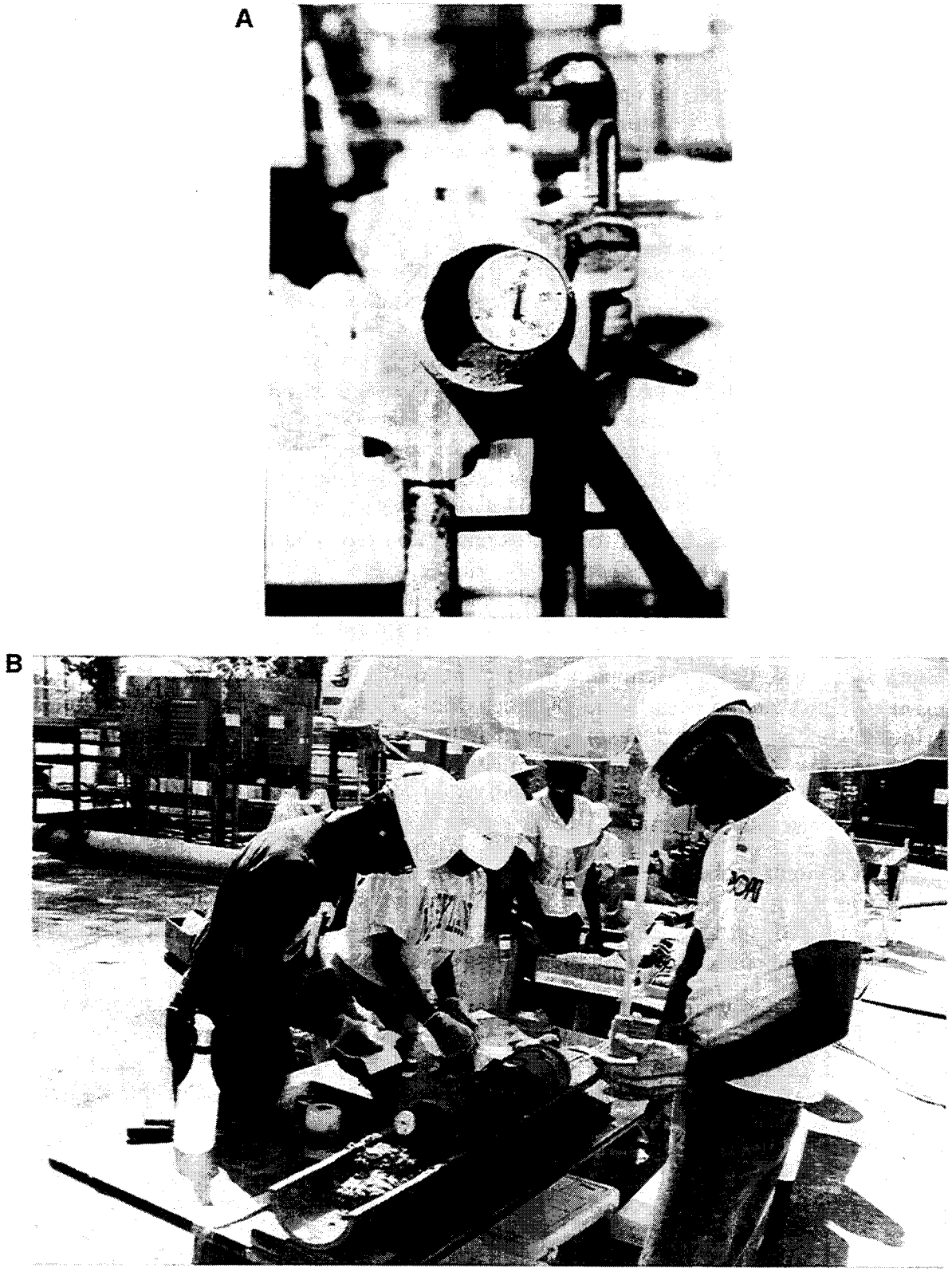

Figure 2. Temperature probe inserted into: (A) split spoon sample, (B) continuous core during DUS sampling at Gasoline Spill site.

were aligned both vertically and horizontally. All temperature, depth measurements, and other sampling details were recorded in a field log book during the drilling and sampling operations. Some cores reached temperatures of approximately 100° C due to the introduction of steam and electrical heating in the subsurface. Heat insulated gloves were worn to handle the hot cores and caution was exercised at all times during the sampling operations. Core temperature data appears in Appendix D.

Quality Assurance/Quality Control Issues

Sampling activities were designed to minimize time between the retrieval of sediment core from the borehole and the subsequent storage on ice of the sample cores identified for analysis, to ensure sample integrity. During sampling for the preliminary characterization, cores retrieved from the boreholes for chemical analyses were immediately pounded into brass sleeves, and covered at the ends with teflon tape and plastic caps, and stored on ice until analysis, to help minimize VOC losses. Additional care was taken with similar core samples during the sampling activities which followed the post steam injection and electrical heating. Once the hot cores were extracted from the boreholes they were quickly wrapped in aluminum foil, temporarily labeled, and put on dry ice to minimize VOC losses. After the samples had cooled to approximately 0°C, they were taken out of the aluminum foil wraps and teflon tape and plastic end-caps put on before the permanent labels were attached. These samples were stored on wet or dry ice in the field as mandated by the type of analysis. Samples intended for later analysis were stored on dry ice in the field and transported to an ultrafreezer (-70°C) for longer-term storage.

Appropriate steps were taken to implement elements of the Quality Assurance Management Plan (QAMP) which were relevant to the DUS activities. Field spikes of surrogate chemicals were performed on bulk thermal desorption chamber (BTDC) samples for estimation of contaminant recovery. Additional samples were collected and analyzed for Quality Assurance and Quality Control purposes. The samples consisted of laboratory duplicates, equipment blanks, trip blanks, and field duplicates.

Background contamination levels associated with sampling and drilling equipment were determined by the collection of equipment blanks. For each borehole, one equipment blank was collected and prepared during sampling activities by rinsing the sampling equipment using standard procedures and collecting the rinsate in glass jars for later analysis.

Laboratory duplicates were used to assess analytical variability. These samples were prepared in the laboratory. Two subsamples for the desired analysis were removed from the same sample sleeve, extracted, and analyzed. In addition, adjacent samples from the center of the sediment core in the core barrel were analyzed by two separate laboratories within 24 hours to validate data integrity.

Laboratory Procedures

Physical Analyses of Sediments

Gravimetric Water Content

The gravimetric water content was determined on an entire soil core. A 150-mm × 75-mm KIMAX glass dish with a watch glass cover was used in this analysis and labeled to resist temperature effects. The head space was recorded before the soil in the brass liner was emptied into the dish. The dish and its contents were covered and placed to dry in a convection oven at 60°C for 48 hours. This drying time was used for uncontaminated soil samples. However, if the dried sample was found to contain volatile organic compounds, then the drying time was extended to 96 hours. The soil was left to cool at room temperature before reweighing. The percent moisture or water content was calculated by dividing the difference between the weight of the soil before and after drying by the weight of the soil before drying, and multiplying the result by 100%. This procedure for the water content expressed on the basis of the oven-dry mass of soil is described by Head (1992). Sample calculations for all of the laboratory procedures mentioned are described in detail in Appendix E of this report.

Bulk Volume

The volume of the brass liner/cylinder was calculated first. The sediment volume (soil bulk volume) was determined by accounting for the height of the sediment in the cylinder relative to the height of the cylinder itself.

Dry Bulk Density

The soil dry weight was divided by the bulk volume to determine the bulk density of the soil; i.e. density = mass/volume.

Volumetric Water Content

Volumetric water content was calculated as a product of the dry bulk density and the gravimetric water content as described by Freeze *et. al.* (1979).

Percent Gravel

Approximately 250 g of dried soil was prepared for transportation to a California State-certified laboratory for further analyses. The remaining portion of the soil (~200 g) was gently ground in a mortar to enable easy separation of grains held together by the silt and clay in the soil. The gravel-fraction of the loosened soil was measured by using a 2.00-mm sieve aperture size (No. 10 sieve). The gravel portion of the soil was weighed and recorded.

Soil pH

An Altex 60 pH meter by Beckman was used in determining the pH of the soil. The meter was calibrated using pH 7 and pH 10 buffers. Using a small spatula, 10 g of dried soil was mixed with enough (~ 10 ml) double distilled water (ddw) to make a saturated paste. The soil paste was left to equilibrate for an hour before the pH was recorded.

Particle Density

Approximately 10 g of oven-dried soil was weighed to the nearest 0.01g and inserted into a clean 25-ml graduated cylinder. Exactly 10-ml ddw was added and the contents shaken to ensure

complete wetting of the sediment particles. An additional 10.0 ml of ddw was added in stages to wash down the sides of the cylinder until all the sediment had dispersed into the water. The new volume of the mixture was recorded and the particle density calculated as the mass of the sediment divided by the displaced volume.

Porosity

Porosity was calculated from the dry bulk density and the particle density measurements and is given by the following equation:

$$\text{Porosity} = \left[1 - \left(\frac{\text{Bulk Density}}{\text{Particle Density}} \right) \right]$$

Sorption Constant (Kd)

BTEX and VOC sorptive properties were also determined in order to better predict contaminant movement and remediation strategies. Laboratory batch sorption experiments were performed on an aliquot of the sediment core sample sent for particle-size distribution. Determinations of laboratory sorption constants (Kds) are based on batch isotherm experiments using C-14 radiolabeled chemicals as described in Bishop et al (1989). The sorbent-sorbate combinations were prepared in triplicate using a solid-to-solution ratio of 0.5 to 1 g/50 mL. Concentrations of test chemical in the solution phase were compared to concentrations in solutions that were treated in an identical manner, but contained no sorbent. The amount of chemical sorbed to the soil was determined by the difference. In preliminary experiments, a series of sorption experiments performed in the concentration range of 50 parts per billion (ppb) to 1 part per million (ppm) resulted in linear isotherms. Hence, sorption experiments conducted on the sediment material from the study areas were performed at one concentration within the linear range, which was typical of contaminant concentration in the localized area. Sorption experiments were performed on samples of aquifer material that had been sieved to <2 mm to remove the gravel. The gravel fraction was assumed to have no sorptive properties; therefore, resulting sorption data were normalized by the percentage of gravel to obtain the reported Kd values. These data appear in Appendix F.

Chemical Analyses of Sediments

Soil samples obtained from each of the sampling locations were analyzed for total petroleum hydrocarbons (TPH, gasoline fraction) by modified SW-846 method 8015, and benzene, toluene, ethylbenzene, and xylenes (BTEX) by SW-846 method 8010; this data appears in Appendix G. The specific method to be used for TPH is a California Department of Health Services method. These methods were chosen in order to be comparable to the analyses which were conducted on the pre-DUS treatment soil samples. These analyses provide a good measure of the performance of the technology in removing the gasoline compounds from the soil, since they are specific to those compounds expected to be present in gasoline. Sample remained sealed in the sample sleeves and were refrigerated at 4°C or below until the aliquot was retrieved from the core. Recovery of sample aliquots from the sample sleeves for all chemical analyses was performed using a manual coring device in order to obtain representative aliquots for analysis (~10-50 grams per sample). The aliquots were weighed directly into a tared gas chromatograph (GC) purge-and-trap apparatus for analysis. All samples were extracted using SW-846 method 5030, purge-and-trap.

Analyses were performed by two laboratories; one is a California state-certified laboratory and the second is our LLNL/ERD analytical chemistry lab (DBCL). Results appear in Appendix G.

Bulk Thermal Desorption Analyses of Sediments

Bulk Thermal Desorption (BTD) is an experimental method being developed for the analysis of soil samples. The current method for analysis of soil samples involves transferring a small aliquot (0.1 to 5.0 g) of a soil core to a SVOA for purge and trap analysis. The BTD process involves purging an entire soil core with helium in a heated oven and trapping the effluent vapors on a volatile organic compound (VOC) trap (which is then analyzed by thermal desorption/gas chromatography). The advantages to be gained by analyzing the sample by BTD are lower detection limits, correction of any sample heterogeneity, and the ability to verify sample integrity through the use of field spikes. Unfortunately, BTD has several disadvantages. The method requires longer analysis time, is more labor intensive, does not allow for replicate samples, suffers from contamination problems, and has a low upper limit of detection.

Advantages of BTD

Lower detection limits (approximately two orders of magnitude) are acheived since we are able to analyze an entire core. Previous method limitations held sample sizes to approximately 5 grams. BTD allows analysis of samples on the order of 400-500 grams. Purge and trap (SVOA) analysis suffers from potential sample heterogeneity since a small subsample is taken from a given core. This problem is averaged out in BTD as the entire core is analyzed. BTD also offers the ability to verify sample integrity through the use of field spikes. A known quantity of a surrogate compound may be added to a soil core at the time of collection. Recovery of the surrogate compound gives an indication of the sample integrity through transportation to the analytical lab, storage, and sample handling.

Disadvantages of BTD

BTD analysis for Total Petroleum Hydrocarbons (TPH) is a time consuming process. Complete recovery of the high molecular weight compounds found in gasoline can take more than 24 hours to achieve. Additionally, note that since the set-up, analysis, and cleaning procedures are more labor intensive than those for purge and trap (SVOA) analysis, the number of analyses possible is limited to one every two days and can quickly create a back-log of samples. Another disadvantage of BTD is that it precludes the running of replicate samples. It would be possible to split a soil core for the purpose of performing sample replicates, but with the time constraints mentioned above, this is not very feasible. The BTD method also suffers from contamination problems which are, as yet, unresolved. And finally, the analysis of 400-500 grams of soil limits the acceptable concentration range. Mildly contaminated soils can saturate the Flame Ionization Detector.

Experimental Section

Bulk Thermal Desorption Chamber (BTDC).

The BTDC is a cylindrical vessel 94 mm in length by 70 mm i.d. It has removable caps at each end which are each held in place by four bolts. Each cap has a port for connection to a vapor

stream, and one of the caps has a septum port for direct injection of analytes into the chamber. The closed chamber is placed into an oven and connected to an influent helium stream by means of quick disconnect fittings. The effluent stream passes out the side of the oven and through a water trap (packed in ice) and then through a VOC trap where the analytes are sorbed. The effluent vapor was collected on VOC traps prepared from 11.5 cm × 6 mm od × 4 mm i.d. glass tubes (Supelco, Cat. # 2-0235) packed with Tenax-GC (60-80 mesh, Alltech Assoc.). A schematic of the BTDC is presented in Figure 3.

GC Apparatus

Analysis of the trapped vapor for TPH was performed using a Dynatherm, Inc. model 850 Thermal Tube Desorber and Dynatherm, Inc. model 851 Temperature Controller coupled to a Hewlett Packard HP 5880A series gas chromatograph (GC) equipped with a flame ionization detector (FID). The tubes were desorbed at 220° C (max temperature ramp setting) for 8 min. The Thermal Tube Desorber unit allows for desorbtion of VOC traps directly to the GC; or for direct injection of solutions or vapors to either the GC or to a VOC trap. A fused-silica column (30 m × 0.53 mm i.d.; 3.0 µm film thickness; DB-624, CAT# 125-1334, J&W Scientific) was employed. The injector and detector temperatures were both 200° C. The gas chromatograph oven was held at an initial temperature of 50° C for three minutes followed by temperature programming to 150°C at 5 deg/min, then to 200° C at 10 deg/min with a final hold at 200° C for four minutes. An HP 35900 Interface transfered the data to an HP 3365 Series II Chemstation (DOS) for data collection, storage and integration.

Standards and Reagents

The sample of gasoline employed to calibrate the method was free product (weathered gasoline) obtained from well GSW-15 in June of 1990 at Lawrence Livermore National Laboratory, Livermore, CA.

Calibrations

Two different methods were performed with similar results. The first involved preparing a working TPH stock solution (10,000 mg/L) in 100 ml methanol (high purity, B & J Brand, Baxter Scientific Products) by addition of 1.36 ml weathered gasoline (density – 0.735 g/ml). Differing amounts of this stock (ca. 0.5-2.0 µl) were then injected directly into the Thermal Tube Desorber/Gas Chromatograph to create a calibration curve.

The second method involved preparing a working TPH stock solution of 1,000 mg/L in 100 ml methanol by addition of 136 µl weathered gasoline. This solution was injected in 5-25 µl aliquots through the Thermal Tube Desorber and collected onto VOC traps (this removes a large portion of the methanol). The tenax traps were then desorbed onto the GC column. Response factors generated by the two different methods differed by ca. 5%.

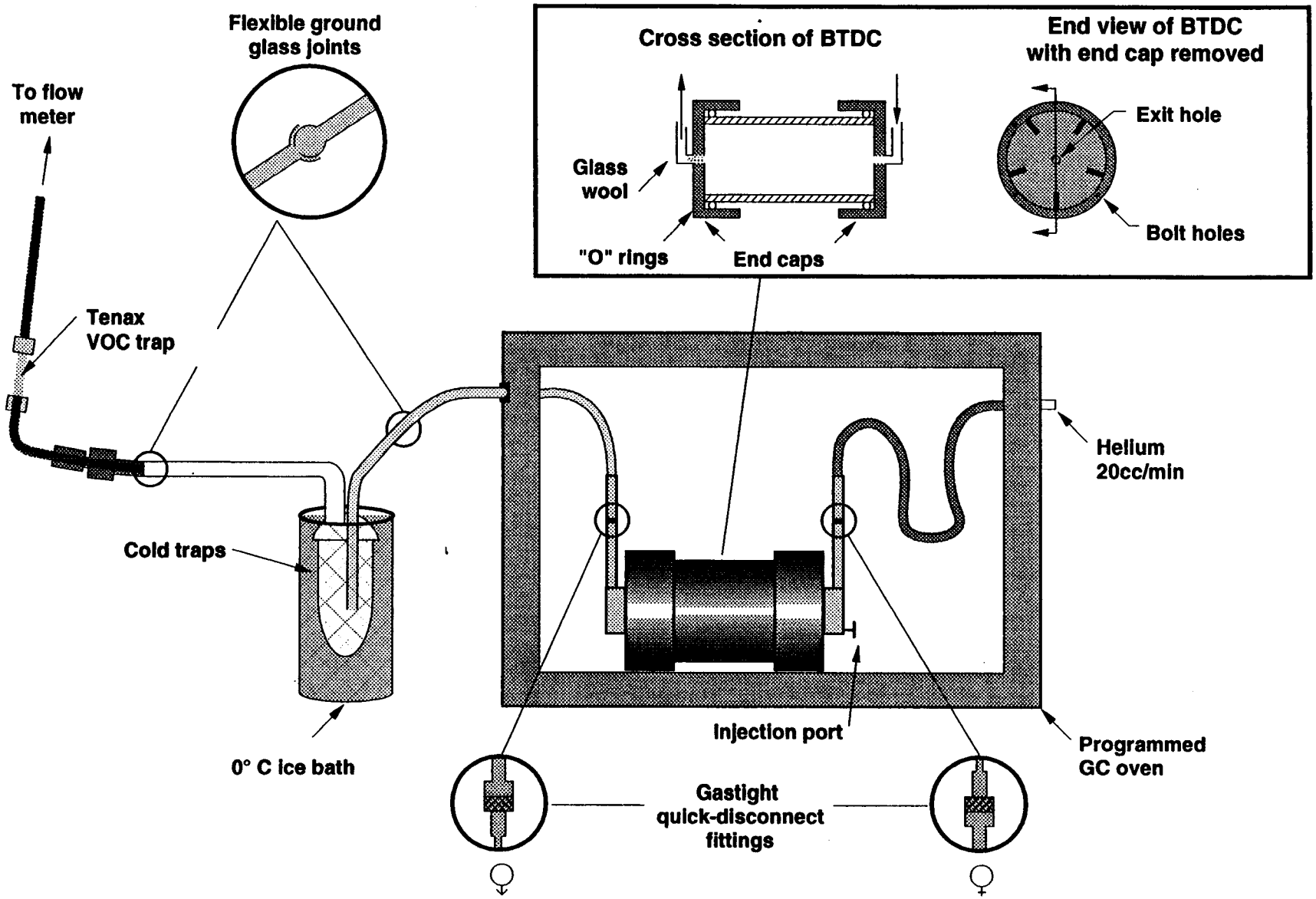

Figure 3. Schematic of the Bulk Thermal Desorption Chamber (BTDC).

This laboratory defines the TPH window as C_6 to C_{12} (n-hexane to n-dodecane). To establish this window, headspace was collected from a vial of n-hexane and injected directly into the Thermal Tube Desorber. The process was repeated for n-dodecane.

Samples

Sample cores received from Treatment Facility F for post-Dynamic Underground Stripping contaminant characterization were stored in a -77 °C freezer. The core samples received were contained in brass sleeves (76 mm × 62 mm i.d.). The cores had a piece of teflon on each end and were capped. The cores were also wrapped in duct tape. To perform a BTD analysis, the samples were first heated slightly to free the soil from the brass sleeve. To accomplish this, the duct tape was removed from a given sample which was then placed into a vinyl glove. This was then placed under warm tap water for several minutes. (Alternately, some samples were warmed by thawing at ambient temperature, approximately one hour). With one end of the BTDC capped the samples were placed on the other end, and the soil pushed from the sleeve into the chamber. The other cap was then locked in place. The BTDC was weighed and then placed into the oven. The effluent line was connected first followed by the helium influent. Flow through the chamber was measured with a bubble meter connected to the end of the VOC trap. Helium flow was monitored and generally kept at 20-30 ml/min. The oven temperature was 175 °C. The VOC traps were periodically changed and the results from analysis of each VOC trap summed to give an overall result. The VOC traps tend to adsorb contaminants during storage. Each one was desorbed on the Thermal Tube Desorber within one hour prior to use.

After approximately two hours purge time the BTDC was removed from the oven and banged on the ground to break-up the soil core. After completing the analysis for a given core, the BTDC was emptied and rinsed with methanol. It was then baked in a 175 °C oven for several hours (generally overnight).

Quality Assurance Measures

Initially, the effluent vapor from analyzed samples was collected on two traps connected in series to check for VOC breakthrough. A significant amount of contaminants was never observed to have been collected on the second VOC trap. In fact, the VOC trap's capacity for adsorbtion of contaminants surpassed the capacity of the FID to measure them.

Prior to running a sample, a chamber blank was first performed to verify that the BTDC was free of contamination. The empty BTDC was heated and purged for one hour (under the same parameters as a sample), and the effluent analyzed. Chamber blanks were performed for each sample analyzed.

Laboratory spikes were performed by injecting a known amount of a surrogate compound to a soil sample through the BTDC septum port. The Laboratory spikes gave an indication of the performance of the BTD system.

Field spikes were added to the soil cores at the time of collection. They were perfomed by making a borehole into a given core with a 21G 1-1/2 inch needle. The surrogate compound was injected into the borehole and the borehole was closed. Field spikes were performed to give an indication of sample integrity through transport and storage.

Core spikes were added to the soil cores in the same manner as the field spikes. They were added in the laboratory after the core had been warmed and was ready for analysis. Core spikes were performed to verify our ability to recover a surrogate compound from a spiked core.

Other Analyses

Several core samples were selected and sent to a California State-certified laboratory for physical and chemical analyses including porosity, permeability, particle size distribution, organic carbon (org C), and cation exchange capacity (CEC). Particle size analysis involved the separation of sediments into gravel-, sand-, silt-, and clay-fractions and were performed by the sieve-and-siphon method of Black (1965). Org C was analyzed by the wet digestion method of Walkely-Black (Hesse, 1971); and the CEC was determined by the ammonium acetate procedure as described by Hesse (1971). These data are presented in Appendix F.

Selected cores were also sent to the LLNL/ERD biology lab for a variety of biological analyses which are described in the biological section of this report.

Results and Discussion

Chemical Data

The compounds used in the soil chemical analyses to do the laboratory spikes were Trichloroethylene (TCE) and Chlorobenzene. The average recovery of the twelve laboratory spikes was 82% (see Appendix G). Ten of the twelve laboratory spikes performed gave recoveries in the 82-102% range. This indicates good overall performance of the system (free from leaks, etc.). In one case (not included in the twelve mentioned above), a laboratory spike was attempted on a pre-heated (90 °C) core. The recovery of this spike was poor (38%), perhaps due to leaks from what was a pressurized system.

The compounds used to do the core spikes were Trichloroethylene (TCE) and Chlorobenzene. Of seventeen core spikes attempted, eleven gave recoveries better than 90%, with an average recovery of 89%. Only once was the recovery of the core spike less than 79%. Twice core spikes were attempted on pre-heated cores (90 °C) in an attempt to mimic field spiking of hot soil samples, and the results were poor (47 and 56% recovery, respectively). This demonstrates that it just may not be possible to reliably spike a hot soil sample in the field.

Due to time and equipment constraints several BTD parameters were not optimized. For example, the column used (DB-624) was not a good one for TPH analysis. It required higher temperatures for reasonable analysis times, and suffered from column bleed at these temperatures.

My personal opinion on BTD is that it is not a good method for TPH analysis. The analysis times were just too long. I think it may have potential, however, if it were used to analyze for volatiles and semi-volatiles (8010/8020 compounds). The BTEX compounds were observed in general to be "completely" stripped from the core in four hours (some of the high molecular weight compounds found in gasoline take 24 hours or more). Unfortunately, we did not , at that time, have the resources to dedicate the proper instrumentation (PID/ELCD) needed to perform

this type of analysis. TPH values ranged from 5 to 87 mg/kg and appear in Appendix G. The highest concentrations are in cores collected closest to the water table. Small concentrations were observed in cores from depths of 40-70 feet that showed non-detect by EPA analysis methods.

Physical Data

The pre-1993 sampling and analysis efforts provided details for preliminary characterization which was used to facilitate more effective planning of borehole locations, borehole completions and design of steam injection locations for the Dynamic Underground Stripping activities.

The locations of boreholes associated with the DUS activities are shown in Figure 1. The approximate extent of the Pre-DUS 1ppm benzene plume in the ground water is also included. The injection wells were located at the perimeter of the 1ppm benzene plume as shown in Figure 1. This was approximately 60 feet from the plume center. The screened intervals for steam injection were determined based on lithologic descriptions of continuous core from the injection boreholes, physical measurements performed on sediment cores from adjacent boreholes (Appendix F), and hydraulic pump tests performed at the GS site (Noyes, pg. 25-29 "Geologic Characterization Section").

A team of people representing the Enviromental Protection Agency (EPA) and DUS management, including the sampling team, worked together to plan the locations of the post-characterization boreholes. Subsequently, the plan was presented to a peer review committee comprised of representatives from DOE SAN and LLNL management. Two boreholes were selected near the outside perimeter of the plume to ascertain whether any part of the plume was pushed outside the injection well boundary during injection of steam. Additional boreholes were planned to evaluate the contaminant mass removal close to the center of the plume. It was decided to plan the boreholes along the B-B' cross-section of the plume that appears in Figures 1 and 4 and is described in more detail in the geological section of the characterization report (Noyes, pg.7 "Geologic Characterization Section").

Results shown in Table 2 verify the appropriateness of the location of the various zones used in the Dynamic Underground Stripping project. The steam zones or zones of higher permeability which comprise mainly sands and gravels, and the electrically heated zones comprising mainly silts and clays are described in Table 2. Descriptions appearing in Table 2 have been separated into results from pre- and post- DUS characterization efforts. The permeabilities listed in Table 2 are averages for each zone; in some cases measured permeabilities within the study area vary over five orders of magnitude (1.0E-08 to 2.8E-03). Subsurface sediments in the GS area are very heterogeneous and lenses of clay materials were found in some of the more permeable zones as evidenced in Figure 4. A comparison of the depths of the confining layers during the pre- and post-DUS phases of the operation tend to show the confining layers in the post-DUS phase at a lower depth than those measured during the pre-DUS characterization phase. This could have resulted from settlement of the coarse sediment material caused by some fines being removed by the steaming process, since a significant amount of fine sediment material was found in the effluent streams.

A contoured map of sediment gasoline concentration is presented in Figure 5. This demonstrates the extent of the contaminant plume prior to DUS activities. The somewhat bell-

shaped plume shows gasoline concentration ranging from less than 1 ppm to greater than 1000 ppm. Two distinct high-concentration zones at depths of 40 and 80 feet are apparent in the plume. The two zones are located approximately in the center of the plume with the lower zone appearing somewhat continuous from the 80-ft through 120-ft depths. The upper high-concentration zone is relatively small and extends from about 35-ft to 50-ft in the subsurface. A table containing BTEX concentrations in sediments retrieved from the study area appears in Appendix G.

Table 2. Description of steaming and electrical heating zones

	Depth (ft)	Description	Gravel/Sand (%)	Silt/Clay (%)	CEC (meq/100 g)	Permeability (CM/s) × E-07
Pre-DUS	64-78	Upper confining layer	38	62	22.6	10.6
	80-110	1st permeable[a] zone	71	29	13.1	5864
	112-120	Middle confining layer	39	61	23.7	2.8
	120-134	2nd permeable[a] zone	73	27	11.9	9291
Post-DUS	77-83	Upper confining layer	48	52	18.9	24.0
	88-112	1st permeable[a] zone	76	24	10.7	7208
	113-118	Middle confining layer	39	61	12.2	3.9
	119-132	2nd permeable[a] zone	75	25	10.2	142.2

[a]These are the permeable intervals used for steam injection.

Figure 6 is a similar contour map which illustrates the gasoline concentrations remaining following the DUS activities. It appears that nearly all of the contaminant has been removed above 85 feet and the remaining contaminant is primarily bounded by the two permeable zones used for steam injection.

In Figure 7, the contoured subsurface gasoline concentrations existing prior to and following the DUS activities are shown superimposed so that a lateral and horizontal removal of the contaminant is more clearly defined. It appears that the northern edge of the plume was more successfully removed than the southern edge of the plume.

Contaminant concentrations in boreholes located at the southern edge of the plume along the B-B[1] cross section appear in Figure 8. Data from GSB-802 (Appendix E) show gasoline concentrations as high as 250 mg/kg within the upper permeable zone prior to DUS activities. Data from HW-102 reveal no significant levels of gasoline present following DUS operations. This borehole is close to 20' south of GSB-802 and the absence of gasoline in this borehole indicates that it is unlikely the gasoline plume was pushed south beyond the injection well at this location.

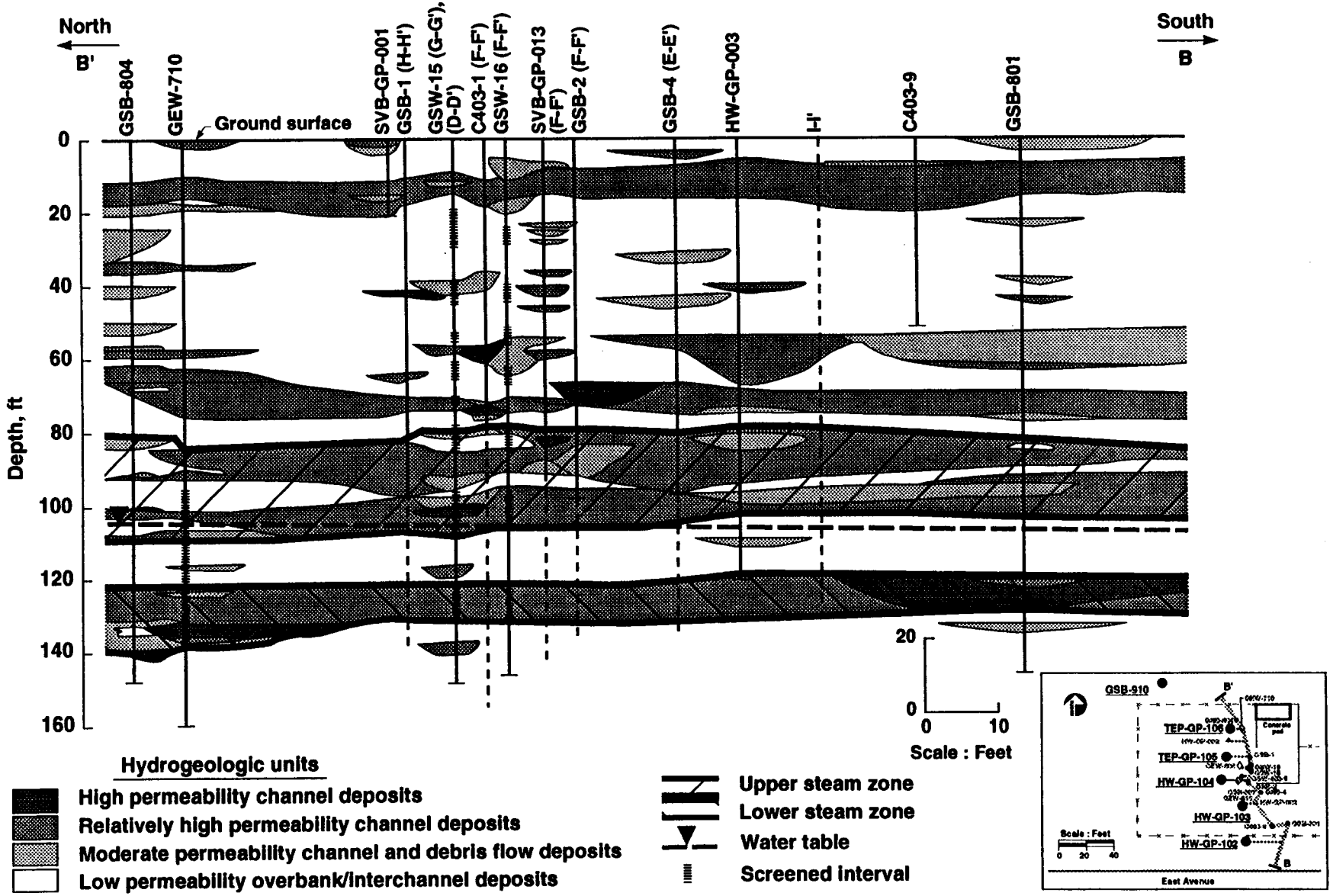

Figure 4. Hydrogeologic cross section B-B' of the Gasoline Spill Area.

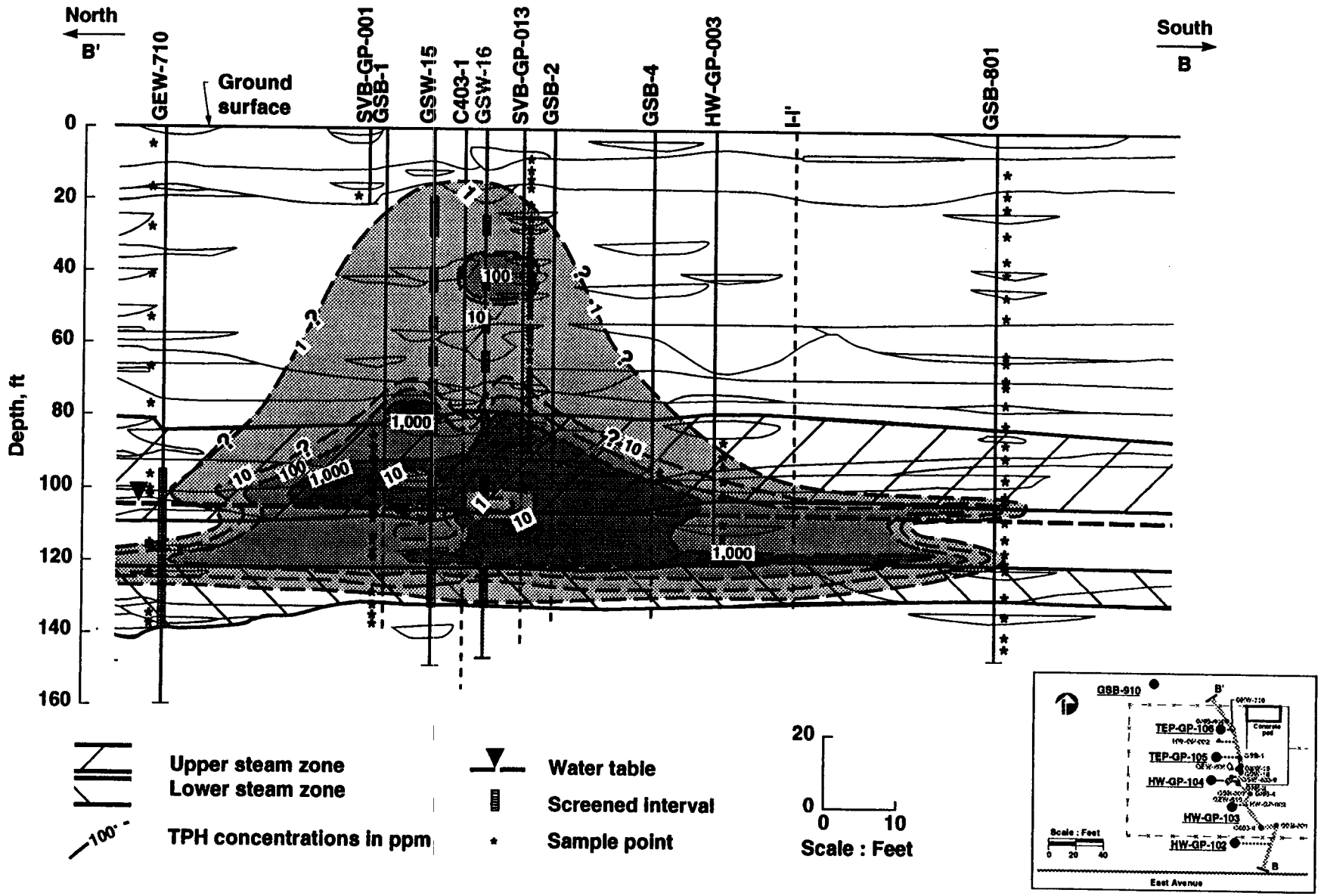

Figure 5. Pre-DUS contoured gasoline concentrations reflect the heterogeneity of the subsurface.

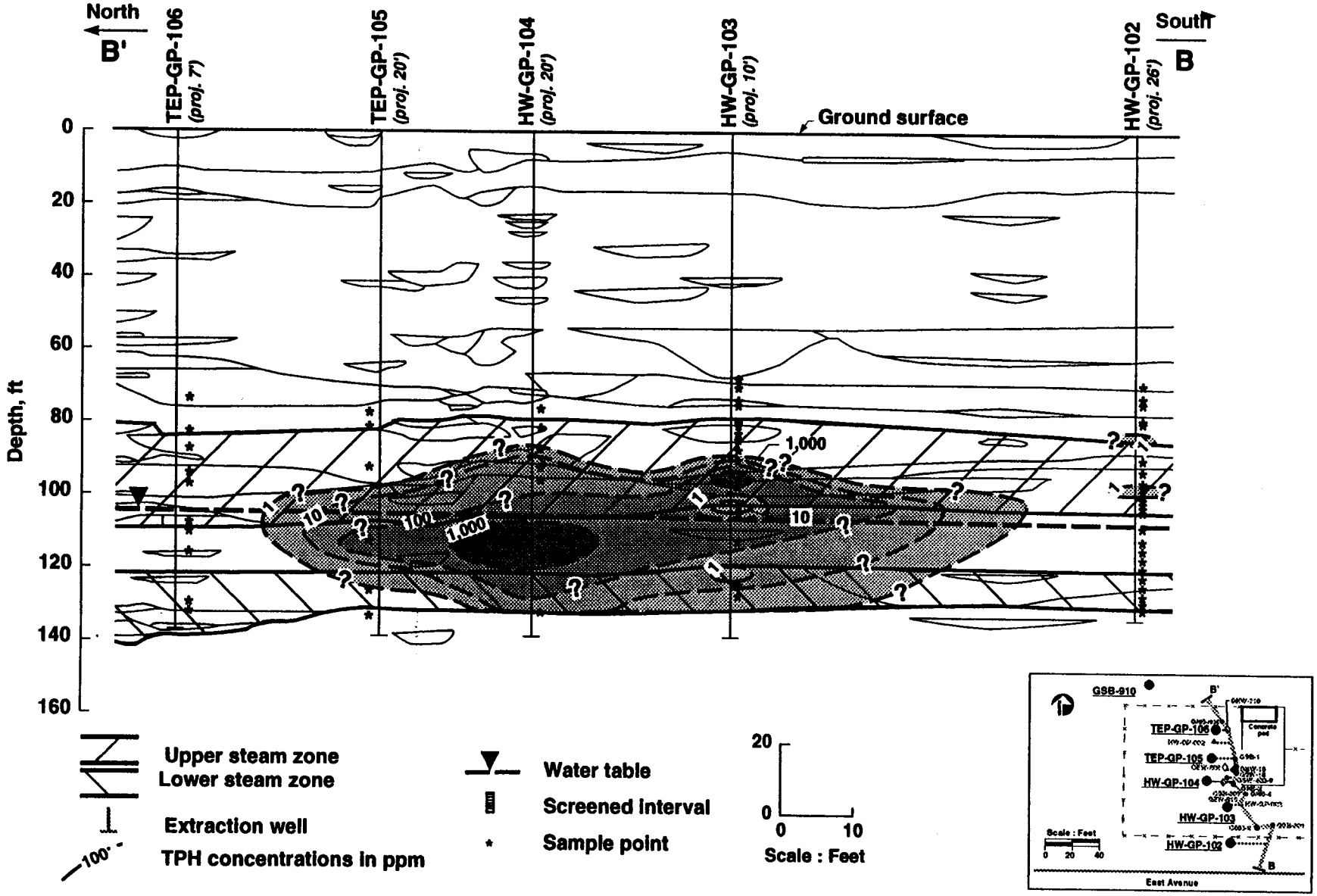

Figure 6. Post-DUS contoured subsurface gasoline concentrations demonstrating the successes of DUS and reflecting the need for further electrical heating.

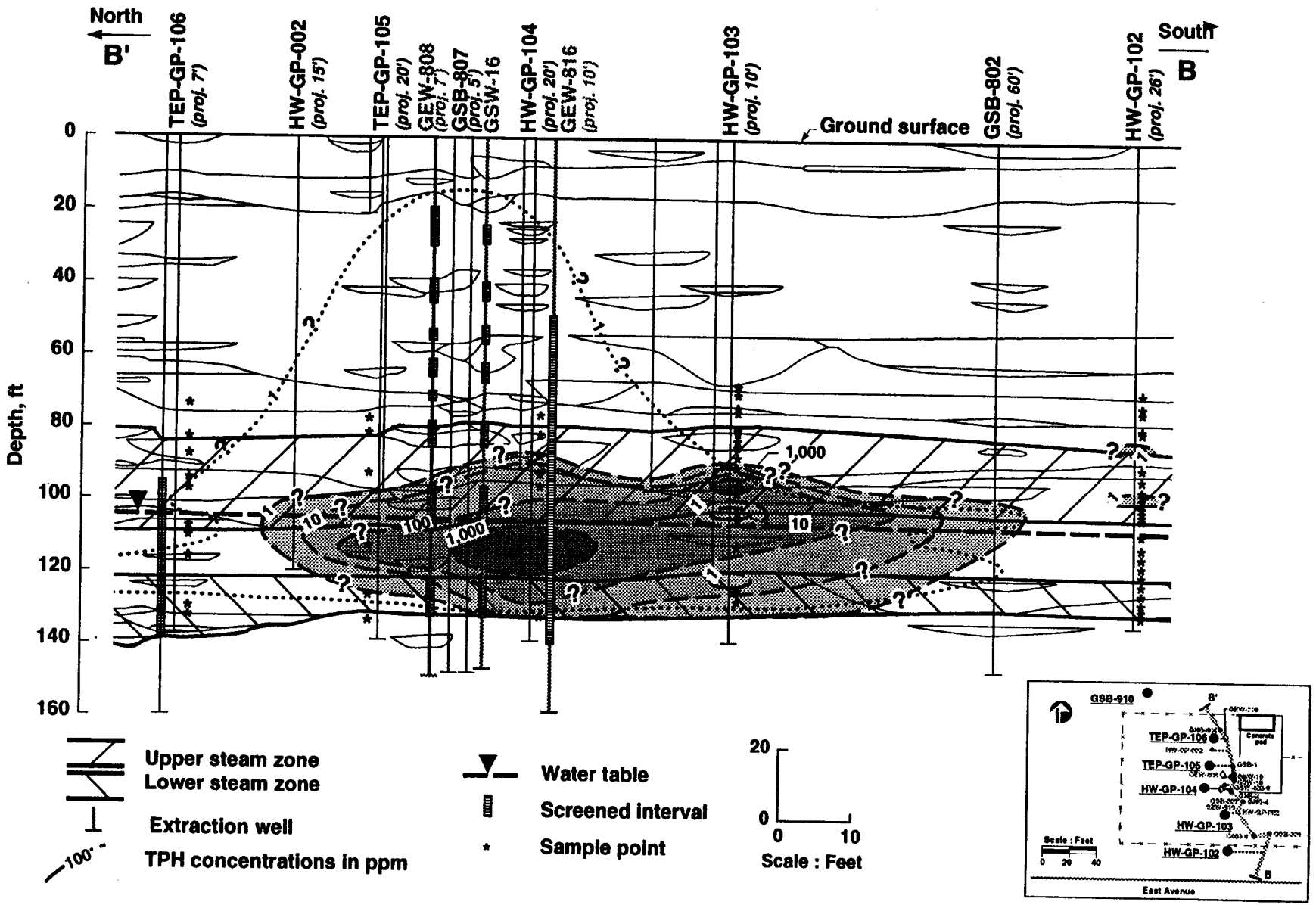

Figure 7. Comparisons between Pre and Post-DUS contoured subsurface gasoline concentrations demonstrating the successful removal of gasoline at the Gas Pad.

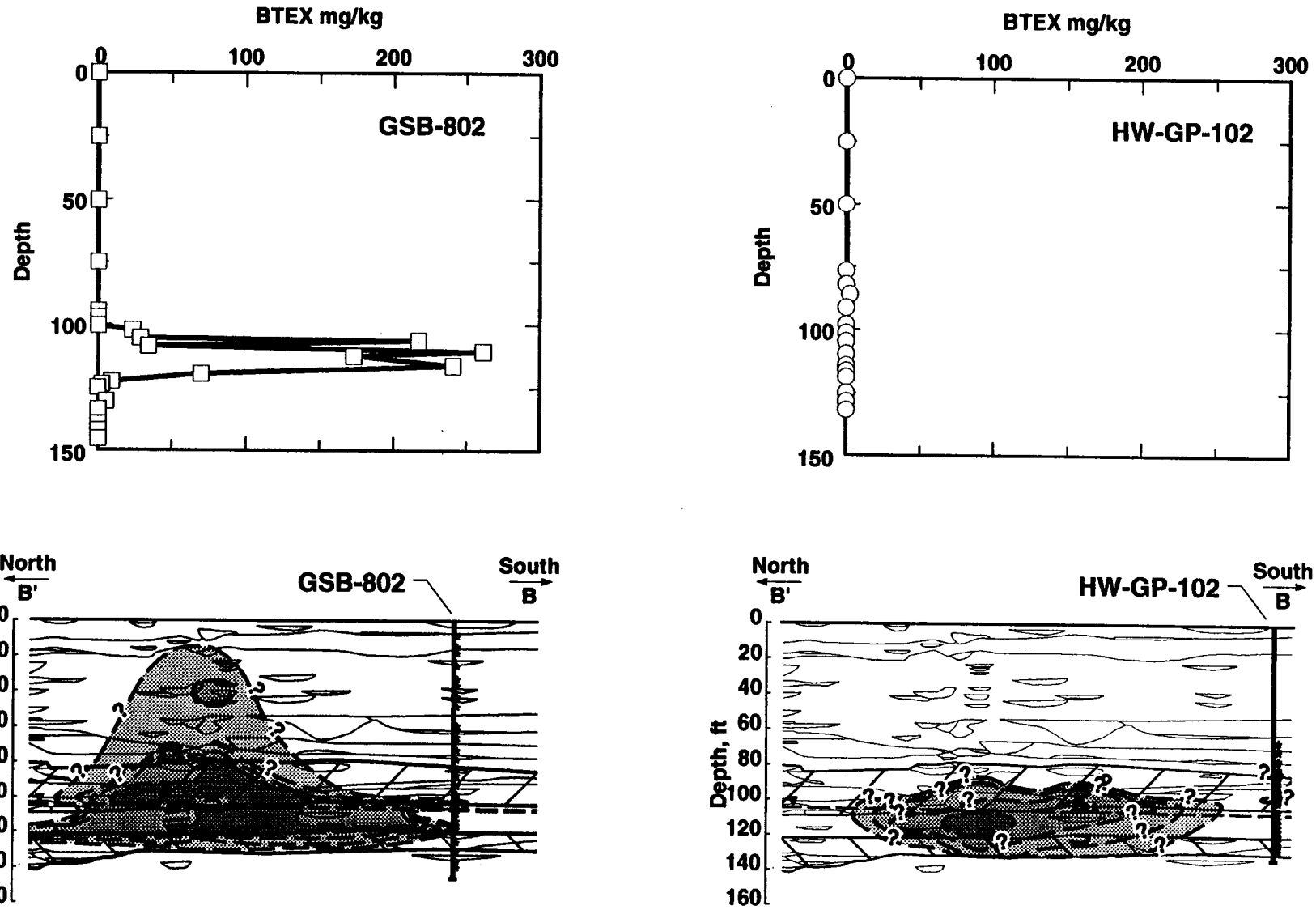

Figure 8. Comparison of GSB-802 (Pre-DUS) and HW-GP-102 (Post-DUS) suggesting that free product gasoline plume was not pushed beyond the perimeter of the injection ring at this location.

The data presented in figures 9 and 10 illustrate the reduction of the contaminant concentrations near the center of the plume where the concentrations were greatest. The upper contaminant zone which was described earlier, and shown near GSB-807and GSB(GEW)-808 has been completely removed as illustrated by the data from boreholes HW-GP-104 and TEP-GP-105. The extent of the plume observed in the lower contaminant zone shown in GSB-807 and GEW-808 has been considerably reduced by the DUS remediation processes as shown near boreholes HW-GP-104 and TEP-GP-105. The plume now resides in a region between depths of 100 ft to 120 ft as illustrated in borehole HW-GP-104 and TEP-GP-105. Even the 1ppm edge of the plume which extended from a depth of approximately 20 ft to 125 ft below the subsurface is now confined to a lesser region at approximate depths between 90 and 125 ft.

The data from TEP-GP-106 as shown in Appendix G validates that there was no contaminant north of the plume. Here again, as in HW-GP-102, it has been shown that the contaminant was not pushed outside the perimeter of the injection wells.

A summary of the analytical results shows a net contaminant mass removal at the study site which appears to be as a direct result of the DUS activities. For more detailed information on mass removal, refer to operations section of DUS report. Additional sediment data show decreases in Org C, CEC and Kd values in some post-DUS boreholes. Earlier characterization reports (Bishop *et.al.*, 1991) on similar data from other LLNL sites show correlation between Kd and clay content in sediments. Statistical analyses are being performed on the data for other trends and correlations.

Lessons Learned

We feel that some permeable zones were under represented by sediment analyes and it is important that a greater effort be made to collect more samples from the permeable zones; even if those samples are disturbed. This was an extremely difficult task for the sampling team because permeable sediments frequently slid out of the split spoon core barrel before core retrieval was achieved. However, even if this occurs in future sampling projects, specific instructions will be written in sampling plans for the recovery and storage of all unconsolidated soils which would better aid in the estimation of permeabliity values; especially in the sand and gravel zones, and in validation of lithologic descriptions. New methods are being investigated by staff in ERD to retrieve and recover permeable materials from boreholes while maintaining sample integrity.

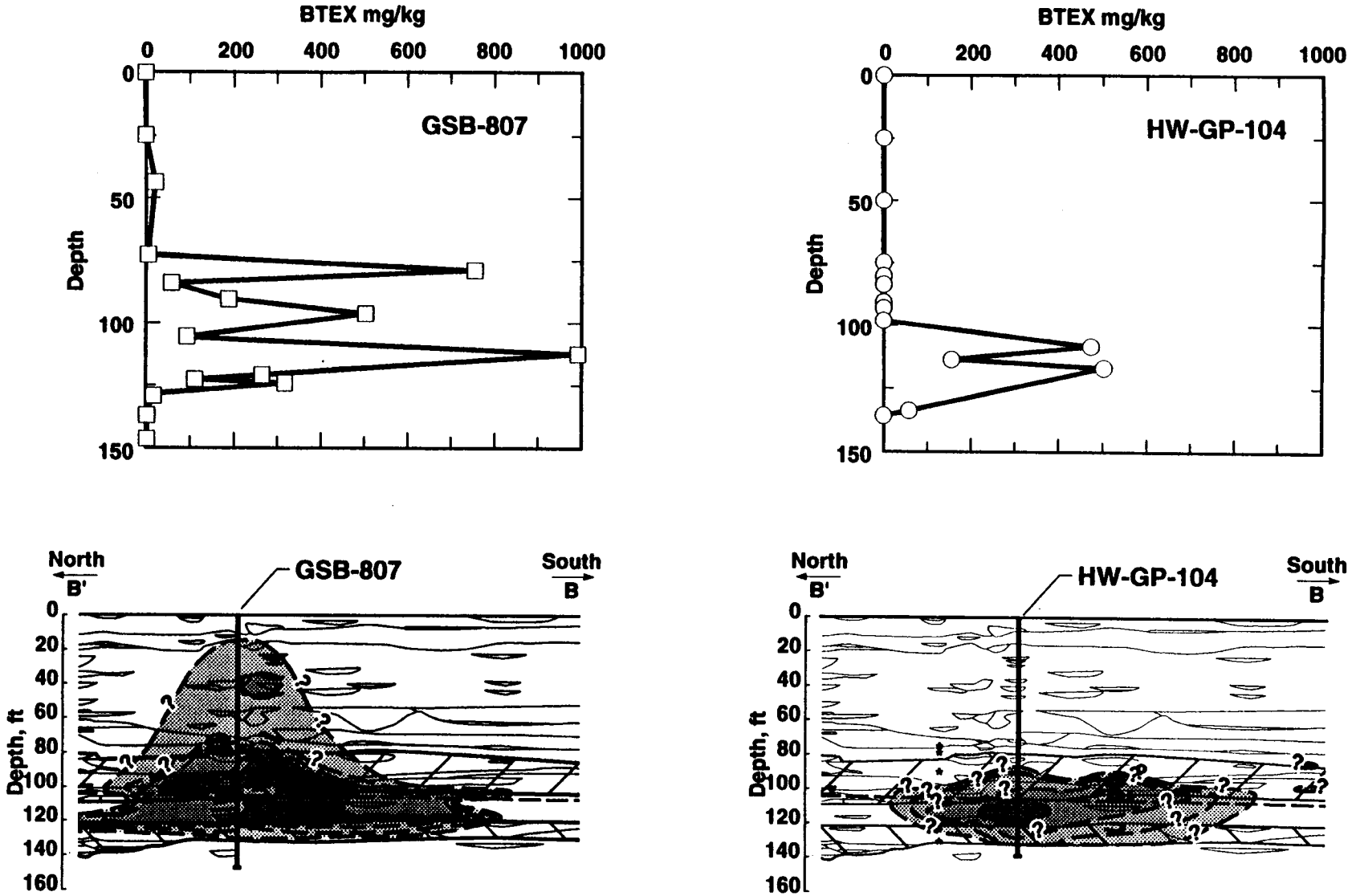

Figure 9. Comparison of GSB-807 (Pre-DUS) and HW-GP-104 (Post-DUS) demonstrating a dramatic decrease in gasoline concentrations in the center of the injection ring.

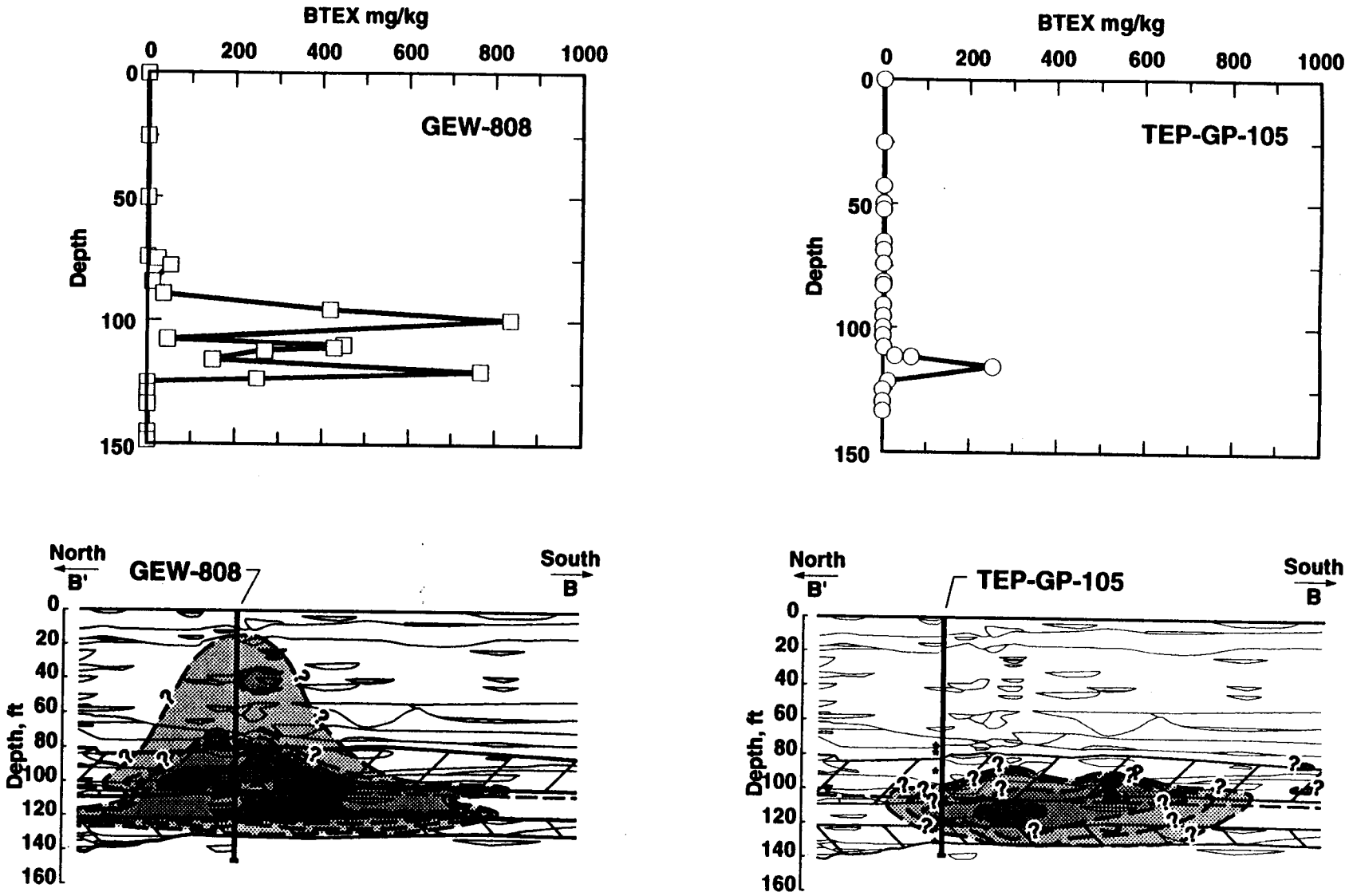

Figure 10. Comparison of GEW-808 (Pre-DUS) and TEP-GP-105 (Post-DUS) demonstrating a dramatic decrease in gasoline concentrations in the center of the injection ring.

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